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M A. Schneller

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BY

M. A. SCHNELLER

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The Coloring Matter of Cane Juices

A PRELIMINARY REPORT

Max A. Schneller, Research Chemist,

Louisiana Experiment Stations.

A process largely used in Louisiana and tropical sugar houses consists in adding small quantities (1 to 3 pounds per 1,000 gallons) of sodium phosphate to the clarified juice in the settling tanks. It is often claimed that this precipitates the soluble calcium salts. W. E. Cross conducted experiments showing that thus but a small fraction of these lime salts could be removed. (La. Bull. 144, pp. 16-18.) He used from 0.2 pound to 1.2 pounds of the salt per ton of cane, equivalent to .01g - .06g per 100 cc of juice for .132g CaO per 100 cc. Calculation alone shows that .565g of crystallized disodium-phosphate are therefore theoretically required. Cross' maximum amount is little more than 1/10 of this and removes in his experiments about 1/10 of the lime. The claimed precipitation of lime salts can, therefore, still less be expected by the amounts practically employed in the sugar houses, which are equal to the minimum used by Cross = .01g per 100 cc. Calcium phosphate is soluble in dilute acids, even acetic. Herewith does not agree the practice of using it at an acidity of about 1.0 cc n/100, while for complete precipitation alkalinity is required. That larger amounts under proper conditions will completely precipitate these lime salts also from cane juice needs no further proof; the following figures on the lime content of juices before and after treatment with sodium-phosphate obtained by titration with Clark's soap solution serve only as an illustration:

CLARIFIED JUICE.

Acidity 1 cc = cc n/100	Alkalinity cc n/100	mg CaO per 100 cc	Treatment, per 100 cc added:
...	0.1	117.5	Untreated
...	0.1	40.5	0.45 g Disodiumphosphate
...	1.0	10.8	0.45 g "
3.8	....	53.0	0.45 g " + 3.8 cc n H_3PO_4
3.6	....	32.5	large excess of " + 3.6 cc n H_3PO_4

.503g Disodium-phosphate are theoretically necessary for complete precipitation of 117.5 mg CaO at slight alkalinity. To effect the removal of lime in the clarified juices of the sugar house, about fifty times the quantity generally recommended would be needed, varying to some extent according to the lime content of the juices.

All that could be claimed for the above process is therefore the creation of a flocculent precipitate, which would tend to carry down fine turbidities not inclined to settle otherwise.

During these experiments it was noticed that the color of clarified juice treated with larger quantities of sodium phosphate was greatly improved. The change in color from the rather dark, blackish tint, which clarified juices acquire on cooling especially near neutrality, to a permanent bright yellow after calcium phosphate precipitation is very marked. The mere removal of soluble calcium salts could hardly produce this change. The addition of large amounts of calcium salts or magnesium salts, which latter are sometimes named as the cause of discoloration in juices (Prinsen Geerligs, Cane Sugar and Its Manufacture, p. 160), produced no further darkening of the liquors. We, therefore, sought the explanation in the removal of iron salt, which, during the heavy sulphitation, might pass into the juices from pipes and tanks. This suggestion occurred to us, especially when noticing the very striking improvement in color of a syrup clarified with sodium phosphate. This syrup, very dark, but quite clear when cold, turned very bright yellow and slightly turbid when brought to boiling. But every effort to separate this precipitate, suspected to be iron phosphate, by hot filtration resulted in a dark filtrate on cooling. Iron determination in the ash (after melting with potassium bisulfate) showed only a very insignificant amount of iron, as the juice had been concentrated in porcelain; and even in blackstrap, where the iron originally contained in the juice and on evaporation dissolved from pipes and effects would accumulate, it amounted to only .065% Fe. The addition of corresponding quantities of ferric salt to clarified juice did not materially increase its dark coloration. Ferric salt added to sucrose or glucose solution produces no similar darkening; therefore, amounts of iron glucosate corresponding to the above-mentioned traces of iron could

not explain the dark color of juices. We therefore sought the explanation in an organic coloring matter, which might be carried down by the voluminous precipitate of calcium phosphate. In sugar refineries this clarification is generally practiced by addition of lime and phosphoric acid to the liquors in the "blow-ups." But much larger quantities would be necessary in sugar houses to take care of the larger amounts of coloring matter present in juices, and the cost becomes prohibitive. We consequently sought for a substitute method of creating a flocculent precipitant which would serve the purpose as well. After various experiments a precipitate of aluminum hydroxid produced by the addition of an alum (Newlands, Sugar, p. 585) salt and sodium hydroxid or milk of lime to very weak alkalinity of the juice (0.5 to 1.0 cc n/100) proved satisfactory. The precipitation of coloring matter seemed to be apparent from the yellowish-brown color of the precipitate. To avoid the introduction of SO_4-ions from the alum into the juice, which, together with the lime added, would cause very troublesome incrustations in the evaporators, we preferred the use of sodium aluminate, of which an addition less than 1/10 per cent of the weight of the juice is quite sufficient to produce a surprising change in color. The juice is heated to near boiling temperature, and the sodium aluminate, dissolved in little water, added. The precipitate, which, besides aluminum hydroxid, also contains lime, probably as calcium aluminate, settles well and is very easily and quickly filtered. The color of weakly alkaline filtrate is by far lighter than that of the original clarified juice. Reacidified to only 0.2 n/100 cc, the juice is of a light straw to lemon color, can be polarized directly without lead subacetate clarification, and remains light yellow indefinitely through concentration to syrup and massecuite, or when allowing the liquor to stand exposed to air for many days.

The process thus developed was to be tested on a larger scale in the Sugar Experiment Station sugar house, when the previously abandoned, but general recognized idea, that iron is in some unexplained manner responsible for the dark color of cane juices, cast doubt on the eventual success of the planned experiment, and caused us to test the influence of iron containers on

syrup obtained by the above method. Nails, well cleaned with HCl and washed with water, were added to the syrup. It darkened within a few minutes. The amount of iron absorbed could only be exceedingly small, but by the Prussian blue reaction it could be easily shown that traces of iron had dissolved, while the light syrup gave an absolutely negative reaction. We determined the quantities sufficient to reproduce the dark color of ordinary sugar house liquors by adding to the yellow iron-free syrup varying amount of ferric salts; to each 33g of syrup 0.1 to 1.0 cc of a solution of 0.86g ferric ammonium sulfate in 100 cc. = 0.1 mg. to 1.0 mg. or .0003 to .003 per cent Fe. The lowest amount produced a noticeable darkening, the highest a dark brown coloration of the bright lemon-colored syrup. Sucrose, glucose and fructose solutions do not react in this manner.

Cane juice, therefore, contains another substance, which causes this reaction. The organic compounds characterized thereby belong to the polyphenols and phenol carbonic acids and usually on the basis of this very delicate iron reaction alone they have been identified in botanical researches as "tannins." But the chemical use of this term is more restricted. The occurrence of "tannin" or polyphenols in sugar cane is not at all surprising, as it is found in practiaclly all the higher plants, and, while its physiological rôle has as yet not been completely cleared, the researches of Moeller, Westermeyer, Kraus, etc., indicate that a certain relation exists between the formation of carbohydrates and tannin in plants. The hyaloplasma, according to Pfeffer and others, is impermeable for sugars in the free state and the migration of carbohydrates from cell to cell must therefore take place with the aid of other substances, the combinations with which are more easily translocated. As such compounds have been regarded the glucosides, especially of tannins. (v. Lippmann, Chemie der Zuckerarten, p. 1770.) Microscopic examination of the cane just before the harvest showed that the eyes, shoots and tops—*i. e.*, the assimilating parts—thus contain polyphenols distributed in the vascular bundles. In the leaves they are found in and near the bundles connected with the stomata; in the top joints of the stalk, where sugar is being accumulated, in the bundles as well as the parenchyma. In the lower joints, where the storage of sucrose has been practically completed, the bundles no longer give the

iron reaction, while in the parenchyma the polyphenols occur sporadically in larger granules, adhering to the cell walls, or as contents of intercellular spaces. The latter fact would indicate a tendency to eliminate the polyphenols as a material which has now ceased to perform a necessary function in the process of sucrose accumulation.

This disappearance of the iron reaction could, however, be explained by a change of these polyphenols into a form which no longer gives this reaction. The so-called incrustating coloring matter of the fibrovascular bundles of cane and all other lignified plant tissues, especially of straw, wood, etc., is thus perhaps a physiological product of polyphenols. Tiemann and Haarman thought this to be coniferin, the glucoside of coniferylic alcohol, a polyphenol derivative which shows no iron reaction. But according to Czapek (Czapek, Biochemie der Pflanzen, Vol. I, pp. 567-9, and Vol. II, pp. 552 and 965), the characteristic reactions of wood with phenol, pyrogallol, orcin, thymol, phloroglucin, etc., and HCl do not exactly coincide with those of pure coniferin. He regards it as an aromatic aldehyde, related to coniferlylic alcohol, which he calls hadromal. It exists in the central lamellae of lignified cell walls in very firm combination, probably as an ester of lignin or cellulose. In agreement herewith is the experience of v. Lippmann, who isolated the coniferin by boiling 2½ tons of alcohol-extracted beet pulp with water for a very long time. The coniferin was so firmly retained that the phenol-HCl reaction did not disappear in the pulp after weeks of boiling. It is, therefore, not probable that the incrustating substance of cane fiber, although producing a very bright yellow color with lime or alkali, could pass into the cane juice to any extent, especially where alkalinity of the juice, containing fine bagasse, is avoided. But as it is colorless in neutral and acid solution and does not produce a dark color with iron, its presence would not be harmful.

Langguth-Steuerwald, however, mentions (International Sugar Journal, 1912, p. 53) this incrustating coloring matter of sugar cane as being possibly the substance causing in combination with iron the dark color of juices, molasses and sugars. He extracted it from bagasse with caustic soda and treated the extract with

Fehling solution (to eliminate the gums), but could not obtain it in crystallized form. He found it to be an aromatic compound, which yielded pyrogallol on dry distillation and catechol on fusion with potash. On heating with mineral acid it split off vanillin. It is evident that by alkaline extraction of bagasse, also, other polyphenols or "tannins" must be dissolved, especially from the eyes. The above reactions, particularly the one with iron, are, therefore, at least partially due to the latter, or to oxidation of the preparation by Fehling solution. The bundles of the cane stalks show the iron reaction after oxidation with alkaline copper solution or chromic acid mixture, which in the case of coniferin would produce vanillin; the latter gives an iron reaction. Langguth-Steuerwald thus sees a resemblance of his substance to phlobaphene, an oxidation product of tannins and polyphenols. He gave it the name "saccharetin" (also used in Prinsen-Geerlig's Practical White Sugar Manufacture, p. 7), which is apt to create the impression that this body is a particular constituent of sugar cane only, while, in fact, it is present in all lignified plant tissues. Czapek (Z. f. physiolog. Chemie, Vol. XXVII [1899], p. 154) obtained his above-mentioned hadromal in crystallized form from wood by treatment with stannous chlorid, extraction of the solution with benzol and purification by the way of its bisulfite compound; it gave all the lignin reactions in intensified form; only when heated it gave off an odor of vanillin. P. Klason (Schriften des Vereins der Zellstoff & Papierchemiker, Vol. II) regards it as a condensation product of coniferylic alcohol and oxyconiferylic alcohol. The color of clarified juice depends on its polyphenol content. In the cane as it goes to the mill the chief source of these are, as already mentioned, the eyes, especially if they have begun to bud. This fact can also be demonstrated microscopically by soaking bagasse in a solution of ferric salt, whereby preëminently the eyes will be stained black. A water extract of the eyes or young shoots gives a very strong greenish black iron reaction. Juice expressed from the (lower) internodes only is much lighter and juice from the nodes only much darker than the juice from the entire cane stalk.

Similar observations may be made also on other plants; thus the rudimentary leaves of the resting wheat germ also show the

phenol iron reaction. The assumption of M. X. Sullivan (J. Ind. Eng. Chem. VI, p. 920) that vanillin is present in wheat germs does not, however, agree with their failure to give the red phloroglucin-HCl reaction characteristic of vanillin. The young tissues of the eyes and undeveloped leaves of sugar cane and the wheat seedling show, of the characteristic color reactions, of the older tissues, only the yellow color with alkali. The phloroglucin reaction does not appear until the leaves begin to assimilate and increases in intensity as the tissues grow older, just in inverse ratio to the iron reaction, the intensity of which gradually decreases and finally disappears with the age of the tissues. One might, therefore, rather assume that the same side-chain of the hadromal, which at first is responsible for the phenol-iron reaction, is gradually changed into a form which corresponds to the pholoroglucin-HCl, but no further to the former reaction.

The lower more mature joints of the cane, showing the phenol-iron reaction to a lesser degree than the immature top joints, produce therefore also a lighter colored juice than the latter. This is easily confirmed by an experiment, and is, therefore, another reason why the tops should be planted rather than ground for sugar production. The occurrence of polyphenols in sugar cane has been only casually mentioned in the literature, no importance being attached to the fact, in the problem of clarification.

W. Krueger, in Zuckerohr und seine Kultur in Java, mentions (page 152) the detection of tannin in sugar cane by Szymanski. C. A. Browne (La. Bull. 91, p. 9) notes the presence of tannic acid in the growing parts and in the peripheral region, especially near the buds and eyes, and (p. 27) he estimates .01 per cent "tannin, coloring matter, etc.," in the cane juice. On page 10 he explains that the well-known darkening of raw juices soon after expression is due to the action of an oxydase and quotes Bertrand, who has explained the darkening of vegetable tissues on exposure to the air by the action of an oxidizing enzyme upon various tannic bodies (Bull. 1896). But, after all, he does not draw the natural conclusion that the dark colored substance thus produced by oxidation is ferric tannate or another phenol-iron compound and that this fact has an important influence on the problem of clarification.

Prinsen-Geerligg asserts in Cane Sugar and Its Manufacture that: "A tannic acid of unknown composition in very minute quantities is present in young canes and in the green tops of ripe ones. The quantity is somewhat insignificant, and combines with albumen immediately after crushing, forming an insoluble precipitate; thus it does not interfere with the further stages of manufacture."

He explains, therefore, on pages 278-280, the dark coloration of some sugars, by an iron saccharate content, but is apparently at a loss to thus account for the color of blackstrap; he thinks here of caramel. In his latest book on Practical White Sugar Manufacture, he again emphasizes the darkening effect of ferric salt on juices due to formation of ferric saccharate (page 8).

But I have explained above that with the small quantities of iron found in juices, iron glucosate or saccharate could never account for such a deep black coloration. It is unmistakably the characteristic iron-phenol reaction, although the quantity of polyphenols present in clarified juice is naturally very small.

From the general occurrence of polyphenol-bodies in plants the presence of these substances should be expected also in the sugar beets, and indeed we find here a similar problem, which, like most facts concerning the beet sugar industry, has been more thoroughly investigated. (A summary on this subject is found in Wohryzek, Chemie der Zuckerindustrie, pp. 104-111.) The fast darkening of freshly expressed beet juice was noticed also here and the chromogenetic substance was shown to be catechol by Gonnermann and Grafe, who detected this polyphenol in beets. On expression of the juice catechol and ferrous salt react and rapidly form the black ferric compound by oxidation from the air or by an oxidase.

After the closing of the grinding season we have no material for the identification of the polyphenol present in sugar cane, but the color reaction of cane juice, greenish black with ferric chlorid and red on addition of sodium carbonate, speaks for catechol or one of its derivatives.

The estimation of these substances by the hide powder method, which, besides the tannins proper, absorb also the polyphenols and their derivatives, would hardly be feasible, but a colorimetric estimation would be applicable.

The means employed in the sugar industry to eliminate the dark color of juices, just explained by the presence of ferric polyphenol compounds, are characteristic reactions of these substances:

(1) Reduction to the colorless ferrous compounds.
(2) Decomposition by acidification.
(3) Decomposition by boiling temperatures.
(4) Decomposition of the ferric phenol compound by slight alkalinity precipitating iron.
(5) Elimination of polyphenols.

The methods 1 and 2 are extensively used in the cane sugar industry. By the action of sulphur dioxide the ferric-phenol compound is reduced as well as decomposed by the mere acidity of sulphurous acid, thus on sulphuring the raw juice. After the elimination of the most of this acid as calcium sulfite, oxidation by air, as well as mere neutralization, cause the return of the dark color. The similar decolorizing effect of other acids employed, as phosphoric, is due only to decomposition by the excess of acid. The acidity permissible for juices is too weak for complete decomposition at ordinary temperature, but its action may be intensified by heating. The liquors, light in color while running hot through the sugar house, darken on cooling and again become light on heating, due to alternate composition and regeneration of the ferric phenol compounds. This phenomenon is more apparent with acids other than SO_2, as then the darkening on cooling due to the restoration of ferric phenol is not retarded by incidental reduction. The above-mentioned (p. 3) very striking change of color of syrup containing phosphoric acid is thus explained. On cooling, the dark color reappears throughout the liquid while syrups acid by SO_2 darken only gradually from the surface on oxidation from the air. As a means of decolorization these methods are very inefficient and contact with air restores the ferric compound, resulting in a dark syrup, a black molasses and a sugar which gradually darkens on oxidation of adhering and occluded traces of phenol-iron. Such a sugar, apparently beautifully white when it leaves the centrifugal, can be easily tested for its keeping qualities if it is treated with NO_2 or Cl in a flask, when such traces will be restored to the ferric state

immediately. The color of the oxidized and the fresh sample may then be compared by the Pekar method (Leach, Food Inspection and Analysis, page 317) as used in flour testing. In a very strange light appear, therefore, all those methods of clarification based on oxidation, employing Cl, H_2O_2 ozone, potassium permanganate, etc. (Prinsen-Geerligs, Cane Sugar and Its Manufacture, p. 184; Noel Deerr, Cane Sugar, p. 251.) Oxidation can only darken sugar house products containing ferrous phenol bodies. In fact, H_2O_2 is the proper reagent to detect their presence. The detection and approximate determination of traces of iron in juice and syrup can be effected by the aid of the Prussian blue reaction—that is, by acidifying and adding an excess of a mixture of ferro- and ferricyanide to react with either ferrous or ferric iron present, or by the sulphocyanate reaction after oxidizing with H_2O_2.

Owing to the sensitiveness of the phenol-iron reaction the dark color of cane juices reaches a maximum with extremely small amounts of iron present, while an increase above this maximum has no further effect on the color. The elimination of iron necessary to effect a permanent clarification must therefore not only be nearly, but absolutely, complete. The above tests reveal that such a complete precipitation of all traces of iron is effected by the described alumina clarification. As alkali salts of fixed organic acids and alkali saccharates prevent the precipitation of iron as hydroxides, phosphates, etc., by the formation of soluble complex iron salts, it is necessary to employ only the slightest excess of alkali. Aluminum hydroxide is much less soluble in sugar solutions than the iron hydroxides and carries down the traces of these which otherwise might remain in colloidal solution or might escape filtration. This reagent proved to be decidedly the most efficient of all precipitants used in these experiments. But the practical use of it in the sugar house is hardly possible in view of the recent strong advance in the price of aluminum salts, which has trebled during the last ten months. Sodium aluminate is obtained as an intermediate product in the manufacture of pure aluminum oxide from bauxite. The crude sodium aluminate liquor we used contained about 28% of solids, of which 6-7% were Al_2O_3, the rest NaOH and Na_2CO_3; it was of dark

brown color, due to organic impurities, which did not, however, interfere with its use for our purpose. As it is not a commercial product, the price it would command lies entirely in the hands of the manufacturers and would likely be higher than that of other commercial aluminum salts. Other flocculent precipitates which, although less efficient, might be used for the same purpose are calcium silicate (which, however, would hardly be filtrable) or calcium carbonate. The warm (50°) clarified juice is limed to about 3-4 cc alkalinity, carbonated back to 0.5 cc and heated to boiling. Filtration is very quick (settling may be used instead); the filtrate is almost as free of iron as that from the alumina process. After resulphuring to acidity it will be necessary to filter off the deposited small quantities of calcium sulfite. This process is perhaps preferable to the alumina method, the drawback of which consists in the deposition on evaporation of small amounts of aluminum hydroxide remaining in the juice in the hydrosol form. The quantities of alkali introduced by the sodium aluminate are, however, no more harmful than the quantities of soluble lime salts it precipitates as calcium aluminate. On further thought, it is evident that the procedure just described corresponds to the double carbonatation process. By the large amounts of calcium saccharate the precipitation of iron is here prevented and takes places only when all the saccharate has been decomposed, just before reaching neutrality. If the carbonation is interrupted at this point (0.5 to 1.0 cc n/100 alkalinity), all iron passes into the precipitate. When carbonating in a single process directly to neutrality the slightest over-saturation would redissolve iron again. Herzfeld (who has investigated the behavior of iron salts in connection with the carbonation process) finds that ferrous salt is thus eliminated more easily than ferric salt, which fact he explains by the isomorphism of ferrous and calcium carbonates. (Z. V. Zuckerind [1895], p. 869; see also Rümpler, Nichtzuckerstoffe der Rüben, p. 463; Wohryzek, Chemie der Zuckerindustrie, p. 362.)

The elimination of iron undoubtedly accounts for the brighter juices usually obtained by the carbonatation process. This feature, as suggested above, could be just as well combined with the sulphitation process. But its advantage must, of course, be

entirely lost again on evaporation in bodies of iron, which sucrose dissolves in neutral, in alkaline and especially in acid solutions. The process would lead to syrups of a permanent light yellow color if the liquors were not allowed to come into contact with iron again. White sugars equivalent to refined products and a very light molasses should thus be obtainable. Louisiana sugar houses operating less than two months could hardly be expected to go to the expense of a copper and brass installation. This may, however, be profitable where, as in the tropics, factories run for eight to ten months of the year, and where, as in Peru, copper installations are already in general use, such a process of iron elimination would be very inexpensive and advisable.

Heating cane juices even to boiling at .05 to .1 cc alkalinity produces no such dark color as usually is feared, provided the alkalinity is only temporary and concentration is effected after reacidification. A destruction of glucose is less noticeable by a loss of reducing power than by the fact that partial reduction of Fehling solution takes place even in the cold and by the appearance of a straw to lemon colored tinge of the juice. Among these decomposition products reducing Fehling solution are also phenols, such as pyrocatechin, protocatechuic acid (Hoppe-Seyler Z. phys. Chem., Vol. 13, 1899; see, also, Czapek, Biochemie der Pflanzen, Vol. I, p. 227; and glucinic acid, which also gives the black iron reaction of the phenols, although its constitution is not known. By heating at higher alkalinity invert sugar solutions are colored dark by glucinic acid, apoglucinic acid and other huminlike decomposition products. On further addition of an excess of milk of lime the color becomes lighter again, the akali salts of glucinic acid having a yellow color (v. Lippmann, Chemie der Zuckerarten, p. 330; also Jesser's researches, Wohryzek, p. 336). Ether extracts these phenolic decomposition products from the reacidified solution; they form a brown syrup from which needles crystallize. The aqueous solution of this substance gives a black reaction which turns to a much deeper brownish black on addition of sodium carbonate; it very strongly reduces Fehling solution. On prolonged heating the glucinic acid is largely destroyed, but the solution produces a dark iron reaction and a slight reduction of Fehling solution in the cold even

then. We therefore have here a second source of polyphenol compounds in processes where the destruction of reducing sugar by heating with lime is practiced; that is, in the beet sugar carbonatation process and its copy in the cane sugar industry, the so-called Battelle process. Considerable amounts of glucinic acid may thus be formed, if the amount of lime added or the temperature of heating are not high enough; and as the lime salts of glucinic acid and its decomposition products are soluble and their reaction neutral, they remain in the juice, causing difficulties in evaporation, much more so, of course, in cane juices with the higher quantities of reducing sugar to be destroyed.

The danger to the color of juices arising from the formation of such polyphenol bodies is at first concealed by the precipitation of iron in the double carbonatation process. But the dark color must reappear gradually, as the metal is redissolved on evaporation in iron bodies. At the low temperatures of 50 degrees to 60 degrees C., usually observed in the cane juice carbonatation process, only small, but still noticeable, amounts of glucinic acid are formed in solutions of reducing sugars; to a minimum extent this is also the case in the above-suggested secondary carbonatation after a primary sulphitation. But if, as in some tropical countries (Cuba) cane juice is evaporated at distinct though slight alkalinity, considerable amounts of glucinic acid, up to over 7 per cent in cane molasses (v. Lippmann, Chemie der Zuckerarten, p. 330), and very dark products must result.

From these considerations it would thus appear best and advisable to avoid alkalinity of cane juices altogether, if iron evaporators, as usually the case, are to be used. The care employed in removing iron by double carbonatation or a similar process would not only be wasted, but more harm may be done by formation of glucinic acid, the amount of which is likely to be far in excess of the small quantities of phenol bodies naturally present in juices. The sulphitation in its present form hardly needs to be improved upon, unless one chooses to use a copper and brass installation. Lining of the iron bodies with rust-proof enamel might prove of some advantage, as it would keep down the iron content and might thus improve the color of the liquors. But

the small quantities of iron naturally found in cane juice and the larger ones introduced with the lime are quite sufficient to produce fairly dark juices, and their elimination needs hardly to be attempted with an iron equipment, only partially protected by enamel.

An iron content of the liquors would, however, become comparatively harmless after elimination of the objectionable polyphenol bodies. Lead subacetate, the clarificant used in sugar analysis, is a precipitant of most polyphenols. Hide powder, specially prepared aluminum oxide and animal charcoal, used in the analysis of tanning materials, absorb, besides tannin, also all the other polyphenols. Only the charcoal process, some time ago discarded in the beet sugar industry, and now limited to refineries, is of practical value. Also vegetable charcoal processes (Norit, Eponit) have appeared; but whether they are as efficient or cheaper than the boneblack process is still an open question. The charcoal process might be of value in the syrup manufacture, where iron precipitation could not be attempted, as alkaline treatment destroys the flavor of the products. For readoption in white sugar houses the ordinary boneblack process is too expensive, but a simpler and more inexpensive modification would be the best and simplest solution of the problem. The destruction of the phenol bodies by oxidation, etc., is not feasible in the cane juice on account of the considerable quantities of reducing sugars present. The majority of such oxidation methods which were mentioned above, are devised rather for beet juices, which, after carbonatation, are quite free from reducing sugars, or for use in refineries after the glucose contained in the adhering molasses film has been removed by washing. Such processes consist in the use of hydrogen peroxide and barium peroxide (Stein and Crossfield), of ozonated air, which is blown through the limed juice (Steffen), of chlorine, the excess of which is removed by acetylene (Kittsee), of chloride of lime, etc. Wöstin (1868) applied lime treatment and carbonatation to the refining process; a similar process is patented in this country.

None of these chemical methods has, however, come into general use in refineries, although the quantities of polyphenols are here only a small fraction of those present in cane juices.

If a compromise between the direct production of the total output of a sugar house as a white product and refinery methods were to be made, the changes would likely be of a physical nature as careful affination of suitable, large-grained raw sugar, and reboiling of the mechanically filtered liquors; i. e., a method to restrict, but not to entirely eliminate, the use of boneblack.

CONCLUSIONS.

(1) The eyes and tops of sugar cane contain polyphenols which pass into the juice.

(2) Traces of iron are sufficient for the production of a very dark color in such juices.

(3) Reducing agents, such as SO_2 and hydrosulfites are only temporary remedies. The dark color returns on oxidation or cooling of juices and syrups.

(4) The dark shade of plantation white sugars, increasing in storage, is due to traces of phenol iron compound.

(5) A permanently light colored juice may be obtained by:
   (a) Complete elimination of all traces of iron and complete avoidance of contact of liquors with iron during further stages of manufacture.
   (b) Elimination of polyphenols by boneblack, vegetable charcoal, etc.

(6) The polyphenol content of juices could be reduced by topping cane low, using tops for planting. This would result in a distinct improvement of the color of juices.